FIELDIANA
Geology

Published by Field Museum of Natural History

Volume 33, No. 7 February 10, 1975

This volume is dedicated to Dr. Rainer Zangerl

Pyritic Cone-In-Cone Concretions

BERTRAM G. WOODLAND
CURATOR OF IGNEOUS AND METAMORPHIC PETROLOGY
FIELD MUSEUM OF NATURAL HISTORY

ABSTRACT

A number of pyritic cone-in-cone concretions from Middle Pennsylvanian black shales of Indiana and Illinois are described. These are the only occurrences of typical cone-in-cone structure composed of pyrite that are known to the author, other than those described from Cambrian and Ordovician shales of the Oslo region, Norway. The Indiana concretions have a core of earthy, phosphatic material, probably coprolitic; the Illinois specimen is an isolated cone. Both occurrences have the typical fabric and structure of the usual calcitic (dolomitic) cone-in-cone. The latter is diagenetic in origin and has formed as a direct consequence of fibrous growth in semi-consolidated sediments. Because of this, the striking similarity of structure between the pyritic and carbonate types, and the contrasts between the crystal habits of calcite and pyrite, the pyritic cone-in-cone is interpreted as a pyrite replacement of original carbonate cone-in-cone concretions.

ACKNOWLEDGEMENTS

The author is grateful to Dr. Rainer Zangerl, who collected four of the specimens discussed here during his field work on black shale fauna in Pike County, Indiana. His genius for suspecting interesting occurrences among ordinary-looking specimens was again demonstrated when these pyrite concretions proved to have excellent cone-in-cone structure and not to be common concretionary masses. My attention was drawn to the fifth specimen by Dr. E. S. Richardson, Jr., who had retained it among miscellaneous specimens brought to Field Museum from the strip mines south of Chicago. The scanning electron microscope (S.E.M.) photographs were taken on a Cambridge S4-10 Stereoscan purchased for Field Museum of Natural History with the help of

Library of Congress Catalog Card Number: 74-28959

National Science Foundation Grant, BMS72-0249 AO1. Thanks are due to Mr. Fred Huysmans for preparing the excellent S.E.M. photographs and to Mr. R. Chavez for aid in preparing specimens.

INTRODUCTION

The nature and origin of cone-in-cone structure have already been discussed in detail by the author in a previous paper (Woodland, 1964). Since then, a number of papers on cone-in-cone have been published. Nearly all refer to fibrous calcite (or dolomite, see Van Tassel, 1971) as the essential element of the fabric. I believe that the growth of the fibrous calcite in particular and rather limited conditions of partially consolidated sediments was directly responsible for the development of the structure.

An exception to this is the epigenetic cone-in-cone calcite found in mineralized and oxidized coal seams in Scotland and the Saar (Mykura, 1960; Bischoff, 1971). Permo-Triassic climatic conditions caused deep alteration in zones of percolation and the oxidative effects produced physical conditions in the residues (analogous to semi-consolidated sediments) suitable for cone-in-cone structures to form when fibrous calcite crystallized in the altered zones.

I did not see papers by Usdowski (1963) and Zaritskiy (1963) before completing my 1964 work. Usdowski's conclusions parallel many of those arrived at by me except that Usdowski considers the fibrous calcite to be a recrystallization of an already-deposited carbonate mud. Zaritskiy considers calcareous concretions with cone-in-cone structure to be late-diagenetic and that the sediments were "appreciably compacted by the time of late diagenesis, under conditions of relatively high pressure" (p. 135).

Gilman and Metzger (1967) conclude that inversion of aragonite to calcite produced pressures causing the conical fractures and the intrusion of clay along the fractures to form the cone-in-cone structure. I rejected this interpretation in 1964 and further studies have only served to confirm my earlier views. Franks' (1969) conclusions on the origin of cone-in-cone structure is in accord with mine.

Cone-in-cone structure in which the matrix mineral is not a carbonate has only rarely been described. Silicified cone-in-cone specimens are interpreted as replacement of calcite, the larger scale cone structure having been preserved while the microscopic fabric was destroyed (Woodland, 1964, pp. 226-229).

Du Toit (1946) had already described cones in amphibole-asbestos seams from South Africa. His description indicates that the structures are virtually identical in essential characteristics to typical calcite cone-in-cone. Du Toit clearly considers the cone structures to be a consequence of the growth of the fibrous amphibole. This occurrence of cone-in-cone structure in asbestos seams reinforces my conclusions on the origin of the more common calcitic types.

In view of this relationship between fibrous habit and cone-in-cone structure, the question arises as to whether other fibrous minerals may give rise to cone-in-cone structure. Fibrous gypsum may be suggested, but no examples are known to me. This may be because fibrous gypsum is usually a late development related to a cycle of weathering rather than to deposition or diagenesis. Under such circumstances the seam is formed within compacted, indurated sedimentary rocks along well-developed bedding planes (or joints?). This results in a clean separation and the seam material produced is a relatively pure gypsum, an inappropriate medium for cone-in-cone and analogous to "pure" fibrous calcite seams (Woodland, 1964, p. 290).

The only other cone-in-cone specimens not composed of carbonate are pyritic, and these are discussed in this paper. The single occurrence of pyritic cone-in-cone described in the literature is in the Cambrian alum shale and Lower Ordovician Dictyonema shale of the Oslo region (Brögger, 1882; Antun, 1967). Brögger clearly considers the fibrous pyrite of the concretions to be replacement of original fibrous calcite (anthraconite) of calcareous concretions. Antun, however, considers the pyrite (both the fibrous portion with cone-in-cone and the coarse-grained masses) to be original, as "associated carbonate concretions show no replacement by pyrite and have a different and quite characteristic outer shell (anthraconite layer)" (p. 218).

Franks (1969) refers to marcasite in disseminated crystals and irregularly-shaped blebs and masses replacing the calcite in cone-in-cone concretions and lenticles in shales of the Lower Cretaceous Kiowa Formation of north-central Kansas. There is no reference to the internal fabric of the marcasite blebs.

DESCRIPTION OF SPECIMENS

Four related specimens (Field Museum numbers G 5286-5289) from one locality and one isolated specimen (G 5301) from a separate locality have been studied by the author. The four

FIG. 1. Approximately vertical broken surface through pyritic concretion, G 5289, in Excello black shale (Desmoinesian, Pennsylvanian), Bethel, Indiana. The central part of the concretion is composed of a dark brown, porous, phosphatic material, probably coprolitic.

specimens are irregular lensoid concretions in the Excello Shale (Desmoinesian, Pennsylvanian) from Bethel, Indiana; their orientations are not known. The largest is approximately 16 cm. long, 6 cm. wide, and 2.6 cm. thick. The cores of three of the concretions are composed of a dark brown, porous, phosphatic material impregnated with fine pyrite. The other concretion in the series has a broad zone (extending across the middle of the vertical section) of pitted pyrite with a small amount of indeterminate matrix. The pyrite appears to have been deposited around more or less spherical centers, which are now voids but which may have

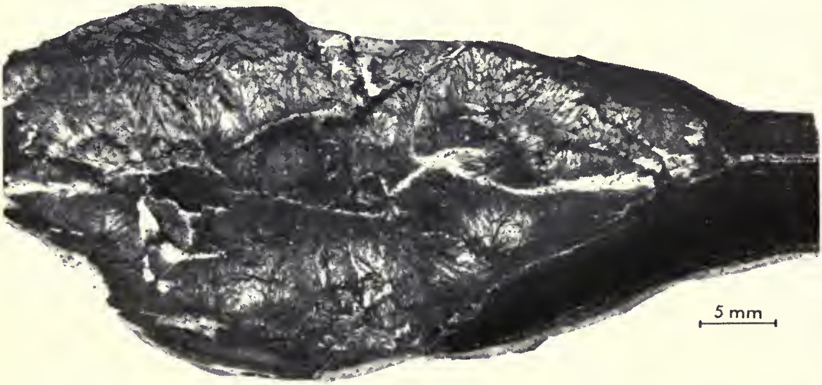

FIG. 2. Polished vertical section of specimen in Figure 1. The central portion is partly coprolitic material and partly epoxy. The partially conical structures are outlined by black shale, and the matrix is dense, fine-grained pyrite.

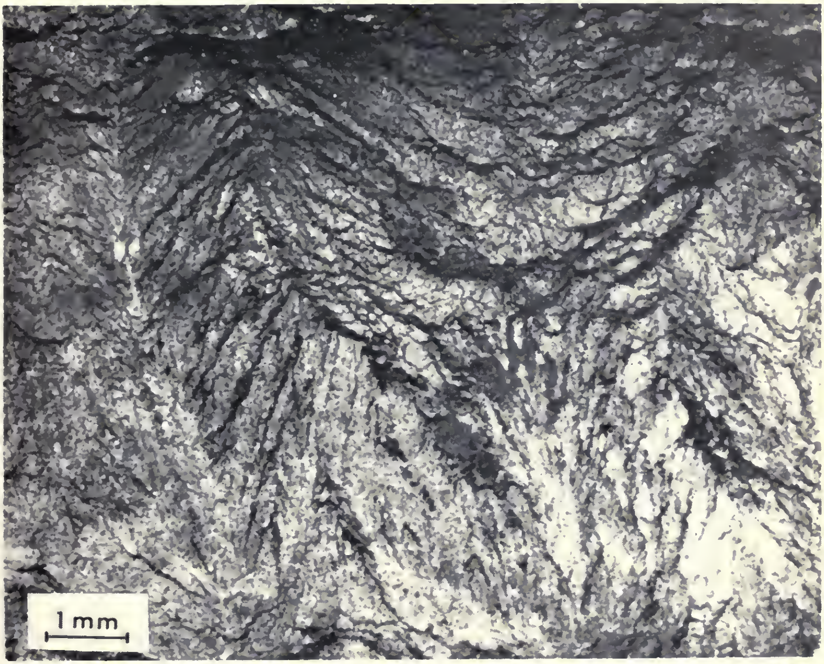

FIG. 3. Enlargement of top left part of Figure 2 showing black shale lenses and partial cone structures in vertical section. Note that the structure is very characteristic of typical calcareous cone-in-cone.

been filled with a soft incoherent material that was washed out during the cutting of the vertical section. The brown material is identical in appearance to coprolitic material. Coprolites occur in Pennsylvanian black shales and have been identified by recognizable organic elements, such as fish scales (Zangerl and Richardson, 1963).

The structure of the pyrite-rich mass is typical of cone-in-cone and is clearly shown in Figures 1, 2, and 3. Shale and, to a much lesser extent, coprolite inclusions occur as lenses and partially conical scales, with characteristic toothed appearance which forms the corrugations on the cones, and are absolutely identical to those in calcitic cone-in-cone. At the margins of the pyrite, wisps and lenses of shale can clearly be separated from the shale mass and penetrating the pyritic mass forming the cone-in-cone fabric (fig. 2, lower right). The pyrite itself occurs as microgranular masses or more massive clots which are associated with thin planar lenses of black shale, but in vertical section under low magnification, particularly where micro-cones of shale are prevalent, it also has

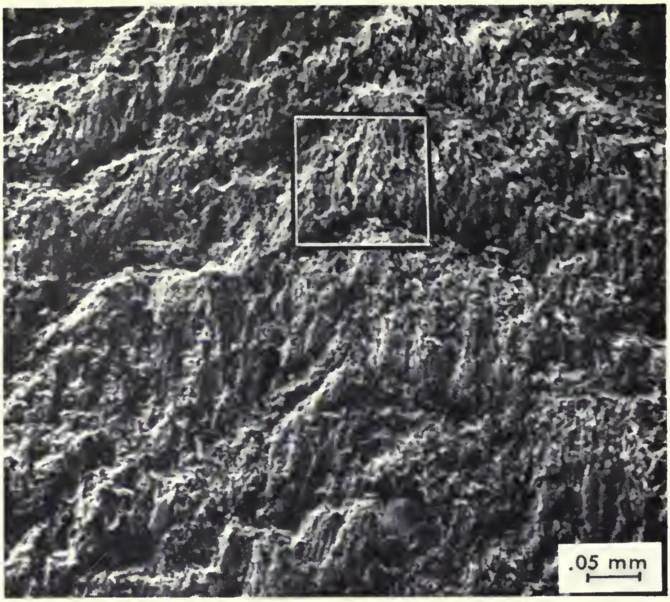

FIG. 4. S.E.M. photograph of smoothed vertical section of pyritic cone-in-cone, G 5286, in Excello black shale, same locality as Figure 1. The arcuate structures are black shale lenses. The pyrite has a more fibrous appearance than in Figures 6-8. Outlined area enlarged in Figure 5.

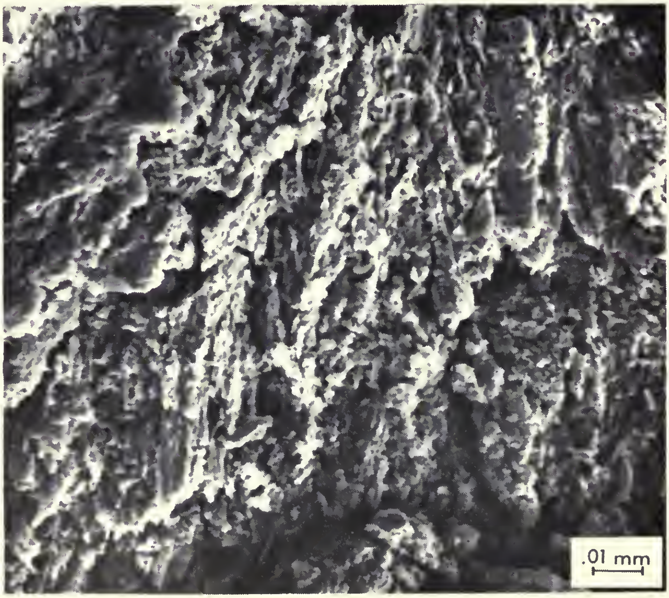

FIG. 5. S.E.M. photograph, an enlargement of the upper center of Figure 4, showing a crude fibrous structure in the pyrite.

the fibrous aspect similar to that of the calcite crystals in calcitic cone-in-cone (fig. 3).

To examine the microfabric of the pyrite, two specimens were prepared for examination by the scanning electron microscope (Cambridge Stereoscan S4). First, a vertical section was smoothed down with #600 carborundum grit, blown clean, and coated. A series of photographs was made; Figures 4 and 5 are representative. A fibrous fabric is apparent, but its relationship to the cone structure is not evident. The presence of many fine lines and wisps of shale forming micro-cone inclusions probably detracts from a clear view of the pyrite fabric.

Second, a near-vertical break was blown clean and coated. A series of photographs (figs. 6-8) from various areas of this specimen shows a varied crystalline structure. Cross striations prominent in Figure 7 at lower magnifications are not nearly so important as the lengthwise fibrous-like appearance in Figure 8 at much higher magnification. The pyrite in this series, however, lacks a fibrous texture that is in any way related to a cone-in-cone structure.

For comparison, Figures 9 and 10 are of a portion of a radially-arranged sub-fibrous to bladed pyrite concretion from Mecca Quarry Shale at Hesler Quarry, Mecca, Indiana. Figures 11 and 12 are vertical sections of typical calcitic cone-in-cone also from Hesler Quarry. The other pyritic cone-in-cone specimen (G 5301) was collected in a strip mine near Braidwood, Illinois. It occurred in black shale, but its orientation is not known. Figure 13 clearly shows its close similarity in structure to typical calcitic cone-in-cone. The pyrite between the shale lenses appears massive, and no fibrous structure is evident even in the scanning electron micrographs (figs. 14, 15).

DISCUSSION

Pyrite is found commonly in Pennsylvanian black shales both finely disseminated and as irregular concretionary masses, including some with radially sub-fibrous texture. This occurrence can easily be explained as the result of high activity of sulfate-reducing bacteria operating on organic material in a marine environment. The environment just below the sediment-water interface would have a neutral to slightly alkaline pH, and be strongly reducing and rich in sulfide. Iron could well have been present, either adsorbed onto or as surface coating on clastic particles. It would be readily released in the ferrous state and would react with hydrogen sulfide

FIG. 6. S.E.M. photograph of a broken vertical surface of pyritic cone-in-cone, same specimen as in Figure 1. Note the triangular pyrite faces. Arrow indicates area enlarged in Figure 7.

produced by bacterial activity to form, first, amorphous iron monosulfide and then, by reaction with elemental sulfur, the disulfide, pyrite (Berner, 1970).

Carbonate concretions also occur within the Pennsylvanian black shales and are occasionally 1 m. or more in diameter. These, again, are consistent with an alkaline pH, possibly enhanced by the release of ammonia by bacterial attack on organic matter. Local CO_2 activity would also be increased by degradation of organic matter.

The major question concerning the pyritic cone-in-cone is whether the pyrite is primary or is a replacement of pre-existing carbonate. The possibility of replacement is attractive because the

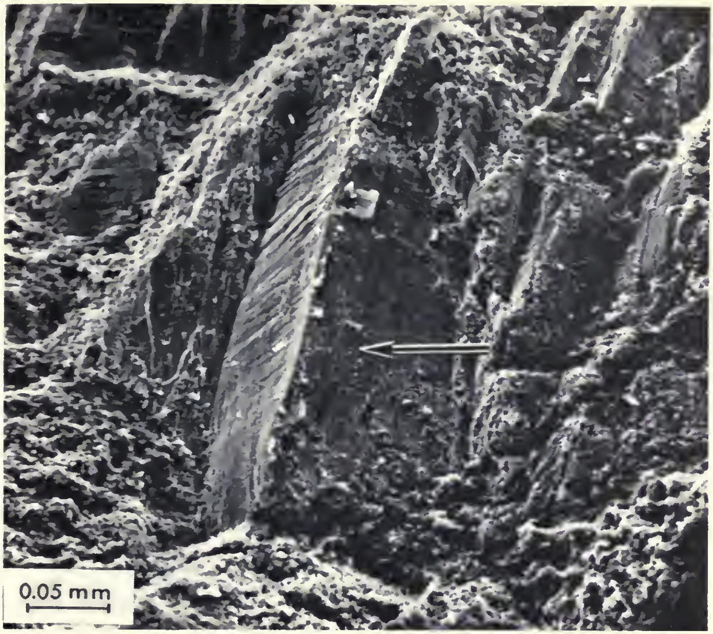

FIG. 7. S.E.M. photograph, an enlargement of the center of Figure 6. Note the horizontal striations on the pyrite faces. Arrow indicates area enlarged in Figure 8.

FIG. 8. S.E.M. photograph, an enlargement of the center of Figure 7. Note that the vertical structure is now predominant.

FIG. 9. S.E.M. photograph of broken surface of bladed spherulitic pyrite concretion from Mecca Quarry Shale (Desmoinesian, Pennsylvanian), Hesler Quarry, near Mecca, Parke County, Indiana. Although spherulitic, there is no suggestion of cone-in-cone structure in this specimen. Arrow indicates area enlarged in Figure 10.

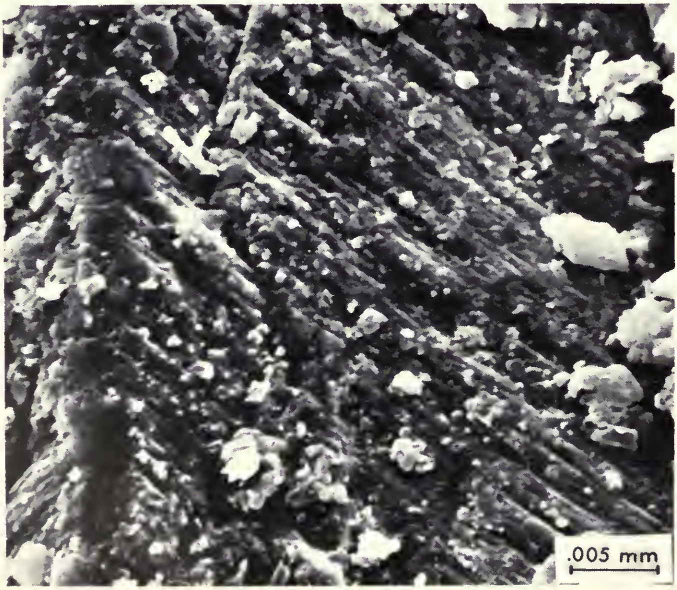

FIG. 10. S.E.M. photograph, an enlargement of the center of Figure 9. Note resemblance to Figure 8.

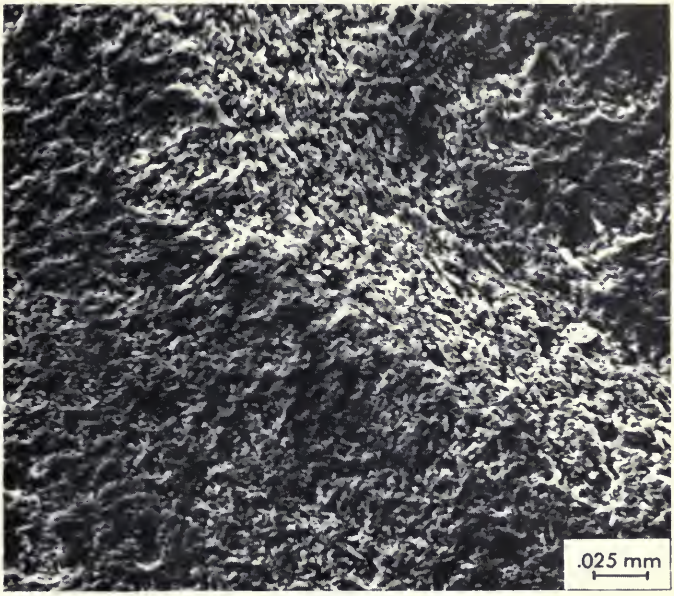

FIG. 11. S.E.M. photograph of smoothed vertical section of calcareous cone-in-cone, G 5294, Velpen limestone (Desmoinesian, Pennsylvanian), same locality as Figure 9. Compare with Figures 4-8.

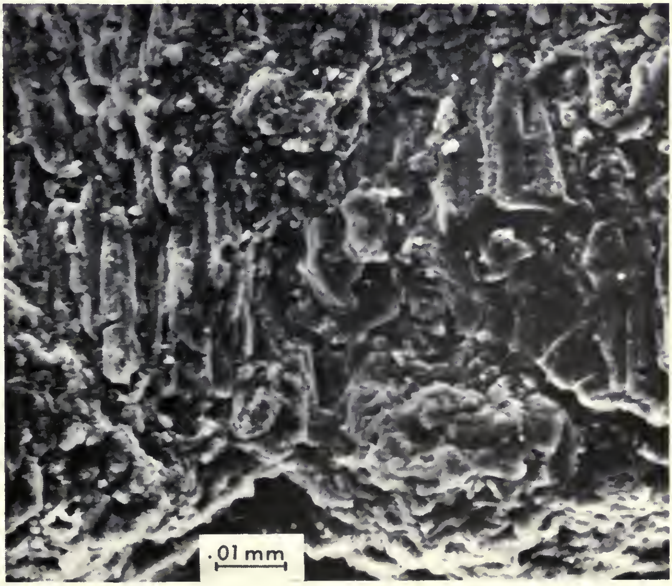

FIG. 12. S.E.M. photograph of broken surface of calcareous cone-in-cone specimen shown in Figure 11. Note the fibrous calcite.

FIG. 13. Polished vertical section of pyritic cone-in-cone, G 5301, from black shale (Desmoinesian, Pennsylvanian), Strip mine 16, near Braidwood, Illinois. Partial cones are formed of black shale. Note that the "dentate" shale lenses at the bottom center are clearly separated and displaced from the horizontal shale at the base by the formation of the cone-in-cone structure.

fabric of the cone-in-cone reproduces faithfully the fabric characteristics of calcitic cone-in-cone with respect to the shale layers, lenses, and conical scales and down to the minutest detail, except for the fabric of the pyrite itself. Also, since fibrous crystallization is basic to the origin of cone-in-cone, a replacement origin is probable. One would not expect the growth of primary pyrite to produce the same pattern as fibrous calcite, having regard to their fundamentally different crystal structures.

As described earlier, some of the pyritic cone-in-cone specimens have a fibrous appearance at low magnifications (fig. 3), but this probably is no more than pseudomorphism of calcite crystal forms. Under high magnifications there is no support for a consistent

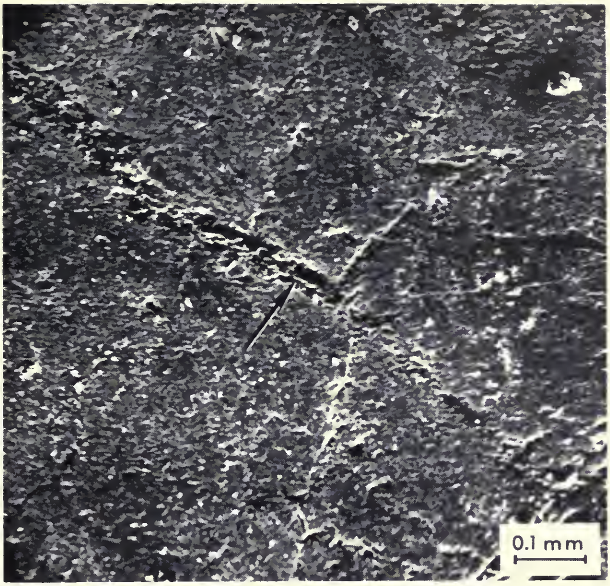

FIG. 14. S.E.M. photograph of smoothed vertical section in pyritic cone-in-cone specimen shown in Figure 13. The v-shaped structure is black shale in partial conical form and enclosed by dense pyrite. Arrow indicates area enlarged in Figure 15.

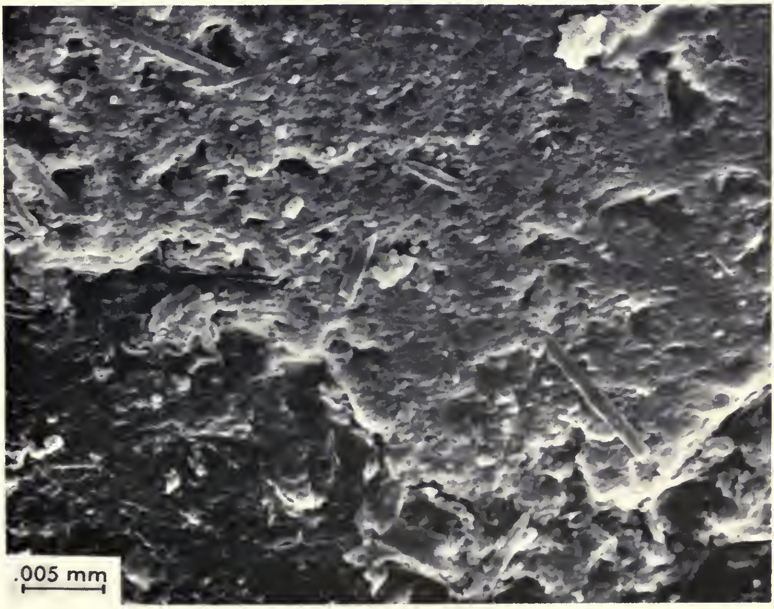

FIG. 15. S.E.M. photograph, an enlargement of the center of Figure 14, showing the contact between pyrite and black shale. Note the lack of structure in the pyrite. The bladed crystals are oxidation products (iron sulfate).

fibrous habit to the pyrite congruent with the axes of the partial conical structures forming the cone-in-cone.

If the pyrite is secondary and a replacement of calcite, there is some difficulty in explaining the order of crystallization. Pyrite occurs very commonly in ordinary calcite concretions both disseminated and in concentrated zones, for example, near the periphery. In many such concretions the precipitation of both the calcite and pyrite is related to the local environment and is the result of the decay of organic matter. Hydrogen sulfide may diffuse outward, react with Fe^{++} ions, and establish a concentration gradient of the latter in a zone around a center of activity of sulfate-reducing bacteria. Simultaneously, calcite would be precipitated in the pore spaces between the clay particles of the mud. In this way a calcite nodule would be formed with zones of pyrite concentration within.

If calcite preceded the pyrite in the cone-in-cone concretion, local activity of sulfate-reducing bacteria would diminish and cease. Presumably, the pyrite was secondarily mobilized from the sediment surrounding the nodule, possibly during the reaction of FeS with free S to produce FeS_2.

In conclusion, the pyrite is here regarded as replacing fibrous carbonate. In part the fibrous habit is preserved pseudomorphously, but, in general, it is not preserved. The gross structure of calcitic cone-in-cone structure established by the clay intercalations both on the macro- and micro-scopic levels is entirely preserved.

REFERENCES

Antun, P.
1967. Sedimentary pyrite and its metamorphism in the Oslo region. Norsk Geol. Tid., **47**, pp. 211-235.

Berner, R. A.
1970. Sedimentary pyrite formation. Amer. Jour. Sci., **268**, pp. 1-23.

Bischoff, L.
1971. Uber einige Flözvertaubungen in Saar-Karbon (unter besonderer Berücksichtigung der Verhältnisse am Merlebacher Sattel). Teil 3, Muntersche Forsch. Geol. Paleontol, no. 19, pp. 1-83.

Brögger, W. C.
1882. Die silurischen Etagen 2 and 3 in Kristianiagebiet und auf Eker, ihre Gliederung, Fossilien, Schichtenstörungen und Contactmetamorphosen. Universitätsprogramme, Kristiania, Norway, 376 pp.

Du Toit, A. L.
1946. The origin of the amphibole deposits of South Africa. Trans. Geol. Soc. S. Africa, **48,** pp. 161-206.

Franks, P. C.
1969. Nature, origin, and significance of cone-in-cone structures in the Kiowa Formation (Early Cretaceous), north-central Kansas, Jour. Sed. Petrol., **39,** pp. 1438-1454.

Gilman, R. A. and W. J. Metzger
1967. Cone-in-cone concretions from western New York. Jour. Sed. Petrol., **37,** pp. 87-95.

Mykura, W.
1960. The replacement of coal by limestone and the reddening of coal measures in the Ayrshire coalfield. Bull. Geol. Surv. Gt. Brit., **16,** pp. 69-106.

Usdowski, H. E.
1963. Die Genese der Tutenmergel oder Nagelkalke (cone-in-cone). Beit. Miner. Petrogr., **9,** pp. 95-110.

Van Tassel, R.
1971. Le constituant carbonaté des concrétions cone-in-cone du Houiller Belge. Bull. Soc. belge Géol., Paléontol., Hydrol., **80,** pp. 21-29.

Woodland, B. G.
1964. The nature and origin of cone-in-cone structure. Fieldiana: Geol., **13,** pp. 187-305.

Zangerl, R. and E. S. Richardson, Jr.
1963. The paleoecological history of two Pennsylvanian black shales. Fieldiana: Geol. Mem., **4,** 352 pp.

Zaritskiy, P. V.
1963. The time of formation of carbonate concretions with cone-in-cone structures. Dokl. Akad. Nauk. U.S.S.R. (AGI translation), **151,** pp. 133-135.